

JCCS Rec'd PCT TO 27 SEP 2005 #4

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

PCT

In re Patent Application of

MAUVEZIN et al

Serial No. 10/539,412

Filed: June 17, 2005

For: PROCESS FOR MANUFACTURING ETHYLENE OXIDE



Atty. Ref.: 4702-19

TC/A.U.: Unassigned

Examiner: Unassigned

\* \* \* \* \*

September 27, 2005

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Sir:

**SUBMISSION OF PRIORITY DOCUMENT**

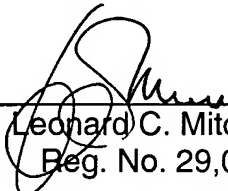
It is respectfully requested that this application be given the benefit of the foreign filing date under the provisions of 35 U.S.C. §119 of the following, a Certified Translation of which is submitted herewith:

<u>Application No.</u>	<u>Country of Origin</u>	<u>Filed</u>
0216145	France	19 December 2002

Respectfully submitted,

**NIXON & VANDERHYE P.C.**

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Application No.: 0216145

Filed: 19 December 2002

VERIFICATION OF A TRANSLATION

I, Nana SEGEDIN,

Director to Malla Translations Limited, of 6 Cameron Road, Bromley, Kent  
BR2 9AR, England declare:

That the translator responsible for the attached translation is knowledgeable in the French language in which the below identified international application was filed, and that, to the best of Malla Translations Limited's knowledge and belief, the English translation of the French application No. 0216145 is a true and complete translation of the above identified international application as filed.

I hereby declare that all the statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the patent application issued thereon.

Date: 4 July 2005

Signature of Director:



For and on behalf of Malla Translations Limited

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# P A T E N T

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The Director-General of the Institut National de la Propriété Industrielle certifies that the attached document is a true copy of an application for industrial property right filed at the Institute.

Drawn up in Paris, 10 February 2003

On behalf of the Director-General of the  
Institut National de la Propriété Industrielle  
The Patent Department Head

[SIGNATURE]

**Martine PLANCHE**

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BR1

**REQUEST FOR GRANT**

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SUBMISSION OF DOCUMENTS DATE 19 December 2002  PLACE  NATIONAL REGISTRATION No. 0 216 145  ASSIGNED BY THE INPI  DATE OF FILING ASSIGNED BY THE INPI Marseilles 19 Dec. 2002  <b>Your file references</b> 9946/B431 (optional)			
<b>Confirmation of filing by fax</b>		<input type="checkbox"/> No. assigned by the INPI to the fax	
<b>[2] NATURE OF THE APPLICATION</b>		Tick one of the 4 following boxes	
Patent application		<input checked="" type="checkbox"/>	
Utility certificate application		<input type="checkbox"/>	
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Conversion of a European patent application Initial patent application		<input type="checkbox"/>	Date .../.../.....
<b>[3] TITLE OF THE INVENTION (200 characters or spaces maximum)</b> PROCESS FOR MANUFACTURING ETHYLENE OXIDE			
<b>[4] PRIORITY DECLARATION OR APPLICATION FOR BENEFIT OF THE FILING DATE OF A PRIOR FRENCH APPLICATION</b>		Country or organisation Date .../.../..... No.	
		Country or organisation Date .../.../..... No.	
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		<input type="checkbox"/> If there are other priorities, tick the box and use the "continuation form"	
<b>[5] APPLICANT (Tick one of the 2 boxes)</b>		<input checked="" type="checkbox"/> Legal entity <input type="checkbox"/> Natural person	
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**BR2**

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The inventors are the applicants		<input type="checkbox"/> Yes <input checked="" type="checkbox"/> No. In this case, fill in the Inventor Certificate form
<b>[8] SEARCH REPORT</b>		For a patent application only (including division and conversion)
Immediate compilation or deferred compilation		<input checked="" type="checkbox"/> <input type="checkbox"/>
Fee paid in instalments (in two instalments)		Only for natural persons filing their own application <input type="checkbox"/> Yes <input type="checkbox"/> No
<b>[9] REDUCTION OF FEES</b>		For natural persons only <input type="checkbox"/> Requested for the first time for this invention (attach notice on non-application) <input type="checkbox"/> Obtained prior to filing for this invention (attach copy of the decision granting free assistance or indicate its reference): AG .....
<b>[10] SEQUENCES OF NUCLEOTIDES AND/OR AMINO ACIDS</b>		<input type="checkbox"/> Tick the box if the description contains a list of sequences.
The electronic data medium is enclosed.		<input type="checkbox"/>
The statement of conformity of the list of sequences on hard copy with the electronic data medium is enclosed.		<input type="checkbox"/>
If you have used the "continuation" form, give the number of attached pages		1
<b>[11] SIGNATURE OF THE APPLICANT OR REPRESENTATIVE</b> (name and capacity of the signatory)		<b>SIGNED FOR THE PREFECTURE OR THE INPI</b> (signature)
Pierre-Dominique LASSALLE – Representative		

**REQUEST FOR GRANT**

**BR/CONTINUATION**

Continuation page No. 1/1

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DATE 19 December 2002

PLACE

NATIONAL REGISTRATION No. 0 216 145

ASSIGNED BY THE INPI MARSEILLES

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**Your file references (optional)**

9946/B431

**[4] PRIORITY DECLARATION OR  
APPLICATION FOR BENEFIT OF  
THE FILING DATE OF A PRIOR  
FRENCH APPLICATION**

Country or organisation

Date .../.../...

No.

Country or organisation

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Pierre-Dominique LASSALLE – Representative

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OR THE INP**

(signature)



**INVENTOR CERTIFICATE FORM** page 1/1  
(To be completed in cases where the applicant(s)  
is(are) not the inventor(s))

This form is to be filled in legibly in black ink DB 113 @ W / 270601

<b>Your file references</b> (optional)		9446/B431
<b>NATIONAL REGISTRATION N°</b>		0 216 145
<b>TITLE OF THE INVENTION (200 characters or spaces maximum)</b>		
PROCESS FOR MANUFACTURING ETHYLENE OXIDE		
<b>THE APPLICANT(S):</b>		
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<b>DATE AND SIGNATURE(S) OF THE APPLICANT(S) OR OF THE REPRESENTATIVE (name and capacity of the signatory)</b>		
(signature)		
P.D. LASSALLE - Representative		

BPCL 9946 / B 431 (1)

The present invention relates to a process for manufacturing ethylene oxide by the catalytic oxidation reacting of ethylene.

5 The catalytic oxidation reacting of ethylene by molecular oxygen leading to the formation of ethylene oxide is known to be strongly exothermic. It is often carried out in a tube reactor, in particular of the “vertical shell-and-tube exchanger type”. In general, the tube reactor comprises three successive and adjacent chambers through which flows a reactive gas current comprising ethylene and molecular oxygen: an inlet chamber of the reactive gas current, then a central chamber, where the ethylene  
10 oxide is formed in a gas current resulting from the catalytic oxidation reaction, and an outlet chamber of the resulting gas current. The central chamber comprises generally a bundle of reaction tubes immersed in a heat exchange fluid and filled with a solid silver-based catalyst. The reactive gas current passes to the interior of the reaction tubes and, by contact with the catalyst, leads to the formation of ethylene oxide in the  
15 gas current resulting from the reaction. Each reaction tube comprises an inlet issuing into the inlet chamber and an outlet issuing into the outlet chamber. In each of the reaction tubes, three successive zones from the inlet to the outlet of the tubes are generally found, that is to say in the flow direction of the gas current, namely a pre-heating zone situated towards the inlet of the tubes, then a reaction zone and a  
20 quenching or cooling zone situated towards the outlet of the tubes.

The desired product of the catalytic oxidation of ethylene is ethylene oxide. However, non-desired secondary reactions may take place, such as complete oxidation of the ethylene and ethylene oxide into carbon dioxide and water,  
25 isomerisation of the ethylene oxide into acetaldehyde and the secondary oxidation of ethylene into formaldehyde. Said secondary reactions contribute to lowering the selectivity of the catalytic oxidation reacting of the ethylene to ethylene oxide.

Several problems arise simultaneously in the manufacture of ethylene oxide.



The most serious problems are linked to the strongly exothermic character of the catalytic oxidation reacting of ethylene to ethylene oxide and to the control of the temperature of the reaction, in particular the whole length of the reaction tubes, from the entry of the reactive gas mixture into the tube reactor up to the exit of the gaseous mixture resulting from the reaction. One of the major risks of the process is the formation of hot spots leading to reaction runaways, known generally under the term “post-combustion”, and to the formation of carbon dioxide, carbon monoxide and aldehydes such as formaldehyde and acetaldehyde, some of said secondary products being particularly difficult to separate subsequently from the ethylene oxide. An irregular reaction temperature profile, poorly controlled and in particular increasing along the whole length of the reaction tubes, may lead not only to hot spots, but also to an excessive final temperature. The hot spots and an excessive final temperature affect the selectivity of the reacting to ethylene oxide. In addition, a locally high temperature and an excessive final temperature may be such that they attain a value corresponding to the maximum flammability temperature of the gaseous mixture, and thus cause an explosion.

Solutions have been proposed for partially resolving some of said problems through methods of various degrees of complexity. There is proposed in Australian patent AU 211 242 a process for manufacturing ethylene oxide in a tube reactor consisting of conventional reaction tubes which comprise an inlet zone filled with inert particles such as spheres of alumina and an empty outlet zone. Between said two zones, the reaction tubes comprise a reaction zone filled with a silver-based supported catalyst the concentration of which rises between the inlet and the outlet of said zone. As a result, the catalytic activity increases along the reaction tubes, from the inlet up to the outlet of the tubes, in the flow direction of the reactive gas current. There is proposed in American patent US 5 292 904 a process for manufacturing ethylene oxide in a tube reactor consisting of conventional reaction tubes which comprise a pre-heating zone situated towards the inlet of the tubes and a cooling zone situated towards the outlet of the tubes, said two zones being filled with an inert refractory product such as a refractory alumina. There is proposed in international patent application WO 02/26370 a catalytic reaction process in a tube reactor consisting of

conventional reaction tubes which comprise an upstream portion and/or a downstream portion situated respectively towards the inlet and the outlet of the tubes, said portions containing a heat exchange insert mainly in the form of rods and having a length equal to 1 to 20% of the total length of the reaction tube. When the process is used for the manufacture of ethylene oxide, it is stated that the upstream and downstream portions of the reaction tubes contain the insert, and that the insert contained in the upstream portion may have a length equal to 1 to 10% of the total length of the reaction tube, while the insert contained in the downstream portion may have a length twice that contained in the upstream portion. However, it is noticed that in all cases the catalyst occupies solely the central portion of the reaction tubes and that a not inconsiderable portion of the tubes is thus filled with inert solid materials intended to promote solely the heat exchanges. Thus, a not inconsiderable portion of the conventional reaction tubes is not reserved for the production of ethylene oxide and as a result affects the production of ethylene oxide per unit of internal tube volume available in the reactor.

The process of the present invention is intended to resolve the technical problems described above. It is intended in particular to increase the selectivity of the catalytic oxidation reacting of ethylene to ethylene oxide and the production of ethylene oxide per unit of internal tube volume available in the reactor, and simultaneously to improve the safety of the process in particular as regards the risks of reaction runaway and explosion, by controlling in particular the profile of the temperature of the reaction the whole length of the reaction tubes.

The present invention relates to a process for manufacturing ethylene oxide by the catalytic oxidation reacting of ethylene by molecular oxygen in a tube reactor comprising three successive and adjacent chambers traversed by a reactive gas current comprising ethylene and molecular oxygen, an inlet chamber of the reactive gas current, then a central chamber forming the ethylene oxide in a gas current resulting from the reaction, and an outlet chamber of the resulting gas current, the central chamber comprising a bundle of reaction tubes immersed in a heat exchange fluid and filled with a solid silver-based catalyst in contact with which the reactive gas current

forms the ethylene oxide, each reaction tube possessing an inlet issuing into the inlet chamber and an outlet issuing into the outlet chamber, the process being characterised in that the area of the internal cross-section of the reaction tubes decreases between the inlet and the outlet of the tubes over at least a portion of the length of the tubes and remains constant over any remaining portion.

Figure 1 represents diagrammatically a tube reactor comprising reaction tubes as used in the process of the invention.

Figures 2<sub>A</sub>, 2<sub>B</sub>, 3, 4<sub>A</sub> and 4<sub>B</sub> represent diagrammatically various reaction tubes as used in the process of the invention.

Figure 5 represents a graph linking, on the ordinate, the temperature of the reactive gas current (measured in degrees Celsius) with, on the abscissa, the length of the reaction tube (measured in metres) from the inlet of the tube, said graph being drawn according to the conditions of Example 1.

Figure 6 represents a graph linking, on the ordinate, the selectivity (S) of the reacting to ethylene oxide (expressed in %) to, on the abscissa, the production (P) of ethylene oxide (expressed in tonnes of ethylene oxide per day) in the conditions of Examples 1 and 2 and of Comparative Example 3.

According to the invention, it was found that it is possible to obtain a relatively stable reaction temperature profile the whole length of the reaction tubes, to avoid reaction runaways and to reduce significantly the final temperature of the reaction, while at the same time improving the selectivity and the output of the reacting to ethylene oxide, in particular when from the inlet up to the outlet of the reaction tubes the area of the internal cross-section of the tubes decreases over the whole length of the tubes, or decreases over at least a portion of the length of the tubes and remains constant over the remaining portion. The area may decrease continuously or, preferably, discontinuously, in particular by stages.

The effects sought by the present invention are particularly attractive when the area of the internal cross-section (A1) at the inlet of the reaction tubes is from 1.5 to 12 times, preferably from 2 to 10 times, in particular from 3 to 9 times greater than the area of the internal cross-section (A2) at the outlet of said tubes.

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The effects sought may, in addition, be particularly remarkable in the following conditions. When the decrease in the area of the internal cross-section of the reaction tubes is effected once only over the length of the tubes, either continuously over a portion of the length of the tubes, or discontinuously, more particularly by a stage, it may be effected at the latest (in the flow direction of the gas current) before the last fifth of the length of the tubes which is situated towards the outlet, preferably before the last quarter or the last third or else the last half of the length of the tube which are situated towards the outlet. When the decrease in the area of the internal cross-section of the reaction tubes is effected two or more successive times over the length of the tubes, either continuously over two or more portions of the length of the tubes, or discontinuously, more particularly in two or more successive stages, it may be effected for the first time at the latest (in the flow direction of the gas current) before the last fifth of the length of the tubes which is situated towards the outlet, preferably before the last quarter or the last third or else the last half of the length of the tubes which are situated towards the outlet.

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For example, the reaction tubes may have a length (L) of from 6 to 20 m, preferably from 8 to 15 m, an area of the internal cross-section (A1) at the inlet of the tubes of from 12 to 80 cm<sup>2</sup>, preferably from 16 to 63 cm<sup>2</sup>, and an area of the internal cross-section (A2) at the outlet of the tubes of less than A1 and ranging from 1.2 to 16 cm<sup>2</sup>, preferably from 1.8 to 12 cm<sup>2</sup>.

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The tube reactor is generally of the vertical shell-and-tube exchanger type, that is to say comprising a vertical bundle of reaction tubes. By bundle of reaction tubes is meant generally an assembly of mutually identical and parallel tubes. According to a practical form of the invention, the reaction tubes may have a cylindrical shape and exhibit a circular internal cross-section whose internal diameter (Di) decreases

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between the inlet and the outlet of the tubes over at least a portion of the length of the tubes and remains constant over any remaining portion. Thus, it was found that from the inlet up to the outlet of the reaction tubes the internal diameter ( $D_i$ ) of the tubes may decrease over the whole length of the tubes, or may decrease over at least a portion of the length of the tubes and remain constant over the remaining portion. The internal diameter ( $D_i$ ) may decrease continuously or discontinuously, in particular by stages, from the inlet up to the outlet of the tubes. Good results are obtained in particular when the internal diameter ( $D_{1i}$ ) at the inlet of the reaction tubes is from 1.2 to 3.5 times, preferably from 1.4 to 3.1 times, more particularly from 1.7 to 3 times higher than the internal diameter ( $D_{2i}$ ) at the outlet of said tubes. Remarkable results may also be obtained in the following circumstances. When the internal diameter ( $D_i$ ) of the reaction tubes decreases once only over the length of the tubes, either continuously over a portion of the length of the tubes or discontinuously, in particular by a stage, the decrease of  $D_i$  may be effected at the latest (in the flow direction of the gas current) before the last fifth of the length of the tubes which is situated towards the outlet, preferably before the last quarter or the last third or else the last half of the length of the tubes which are situated towards the outlet. When the internal diameter ( $D_i$ ) of the reaction tubes decreases two or more successive times over the length of the tubes, either continuously over two or more portions of the length of the tubes or discontinuously, in particular by two or more stages, the decrease of  $D_i$  may be effected for the first time at the latest (in the flow direction of the gas current) before the last fifth of the length of the tubes which is situated towards the outlet, preferably before the last quarter or the last third or else the last half of the length of the tubes which are situated towards the outlet.

For example, the reaction tubes of cylindrical shape may have a length ( $L$ ) of from 6 to 20 m, preferably from 8 to 15 m, an internal diameter ( $D_i$ ) which, according to the invention, decreases between the inlet and the outlet of the tubes and which may be chosen in a range of from 12 to 100 mm, preferably from 15 to 90 mm. In addition, the reaction tubes may have an internal diameter ( $D_{1a}$ ) at the inlet of the tubes which may be chosen in a range of from 38 to 100 mm, preferably from 45 to 90 mm, and an internal diameter ( $D_{2i}$ ) at the outlet of the tubes which is less than  $D_{1i}$

and which may be chosen in a range of from 12 to 45 mm, preferably from 15 to 40 mm.

According to the invention, the reaction tubes have an internal cross-section whose area decreases between the inlet and the outlet of the tubes. They may, in addition, have a wall whose thickness is constant or on the contrary varies, for example decreases or increases from the inlet up to the outlet of the tubes (in the flow direction of the gas current). It is possible in particular to use reaction tubes of cylindrical shape which have an internal diameter ( $D_i$ ) which decreases from the inlet up to the outlet of the tubes, for example continuously or discontinuously, in particular by stages, as described previously according to the invention, and which may, in addition, have an external diameter ( $D_e$ ) which is constant between the inlet and the outlet of the tubes and equal in particular to the external diameter ( $D_{1e}$ ) at the inlet of said tubes. In this case, it was found in a remarkable manner that the enlargement of the wall of the reaction tubes from the inlet up to the outlet of the tubes does not affect, or only in an insignificant manner, the effects sought by the process of the invention.

The solid silver-based catalyst used in the present invention may be chosen from among the silver-based supported catalysts capable of catalysing the oxidation of ethylene to ethylene oxide with the aid of molecular oxygen. The catalyst may be chosen from among catalysts comprising mainly of metallic silver deposited on a porous refractory solid support. The support may be chosen from among refractory products of natural, artificial or synthetic origin, preferably from among those having a macro-porous structure, more particularly having a specific surface area (B.E.T.) of less than  $20 \text{ m}^2/\text{g}$ , in particular of from  $0.01$  to  $10 \text{ m}^2/\text{g}$ , and an apparent porosity of more than 20% by volume, more particularly of from 30 to 70% by volume. The most appropriate supports may be those which comprise of siliceous and/or aluminous products (based on silica and/or alumina respectively). For example, the support may be chosen from among oxides of aluminium (in particular those known under the trade reference "Alundum"®), charcoal, pumice stone, magnesia, zirconia, kieselguhr, fuller's earth, silicon carbide, porous agglomerates containing silicon and/or silicon carbide, clays, natural, artificial or synthetic zeolites, metal oxide gel-based materials

containing oxides of heavy metals such as molybdenum or tungsten, and ceramic products. Aluminous products are preferred, in particular those containing alumina of the alpha type, having in particular a specific surface area (B.E.T.) of from 0.15 to 0.6 m<sup>2</sup>/g and an apparent porosity of from 46 to 52% by volume. The B.E.T. method used to determine the specific surface area is described in J. Am. Chem. Soc., 60, 309 – 16 (1938).

The catalyst may contain from 1 to 20%, preferably from 2 to 16% by weight of silver. It may in addition contain at least one metallic promoter agent, in particular chosen from among the alkaline metals, alkaline-earth metals such as calcium or barium, and other metals such as thallium, antimony, tin or rhenium. The catalyst may come in the form of particles having in particular a mean diameter at least equal to 1 or 2 mm and at most equal to half of the narrowest internal diameter of the reaction tubes employed, in particular a mean diameter chosen from a range of from 1.5 to 15 mm, preferably from 4 to 8 mm, for example in the form of spherical or hemispherical particles, rings, pellets or granules. The catalyst may be prepared according to various processes such as those described in the American patents US 3 043 854, US 3 207 700, US 3 575 888, US 3 702 259 and US 3 725 307, or in the European patent EP 0 266 015.

One of the advantages of the present invention is being able to use reaction tubes containing the catalyst over the whole or at least over almost the whole (that is to say more than 95%) of the length of the tubes, from the inlet up to the outlet of the tubes, and more particularly in the zone situated towards the outlet (only one portion at most equal to 5% of the length, situated towards the outlet, is generally occupied by a device for supporting the catalyst charge, such as a grille or spring). Hence, thanks to the particular configuration of the bundle of reaction tubes, a maximum catalyst charge may be employed for the internal tube volume available in the reactor, and said charge is capable of being in addition active for the production of ethylene oxide. Said advantageous results are in addition obtained while at the same time maintaining a high selectivity of the reaction to ethylene oxide and supplying in particular a relatively stable reaction temperature profile over the whole length of the tubes. It

may be possible, however, if it is so desired, to insert into the reaction tubes inert solid materials, or preferably, where applicable, to mix the catalyst with said materials. The inert solid materials may be optionally chosen from among inert particles or solid and in particular hollow inserts, for example of metal or of metal alloy, or of inert refractory product used in particular as a solid inert filling product, for example in the form of powdery, spherical or hemispherical particles, rings, pellets or granules. The inert refractory products optionally used may be of an identical or different nature to those of the supports present in the catalyst. They may be chosen from among the catalyst supports, in particular those mentioned previously, and from among refractory products having in particular a small B.E.T. specific surface area, preferably of less than 0.1, more particularly less than 0.05, in particular less than 0.01 m<sup>2</sup>/g. The refractory products with a small B.E.T. specific surface area may be chosen from among silica, alumina, silicon carbide, alumina and silica mixtures optionally modified by alkaline or alkaline-earth metals, ceramic products, glass-type materials such as sodium polysilicates containing more particularly a stoichiometric excess of silica.

The process for manufacturing ethylene oxide employs molecular oxygen, which may be used in the form of pure molecular oxygen, for example with an oxygen purity equal to or more than 95% by volume, or in the form of air. The reactive gas current which flows through the tube reactor may consist of a gaseous mixture of ethylene, molecular oxygen and optionally one or more other gases chosen from among carbon dioxide, nitrogen, argon, methane, ethane and at least one reaction inhibitor or moderator chosen in particular from among halogenated hydrocarbons such as ethyl chloride, vinyl chloride or 1,2-dichloroethane. In the reactive gas current, the concentration of ethylene is generally as high as possible, more particularly equal to or less than 40% by volume, and it is in particular chosen from a range of from 15 to 35% by volume. The concentration of molecular oxygen in the reactive gas current may be chosen from a range of 3 to 20%, preferably of 4 to 10% by volume. The concentration of carbon dioxide in the reactive gas current is generally less than or equal to 10% by volume, and may be chosen from a range of from 4 to 8% by volume. Methane and/or nitrogen may be used as diluents in the



reactive gas current in order more particularly to reduce the flammability range of the gaseous mixture and to remove it into a zone not used. Thus methane and/or nitrogen may be present in the reactive gas current in a concentration as high as possible. For example, the reactive gas current may contain by volume from 1 to 40% of ethylene, from 3 to 12% of molecular oxygen, from 0 to 10% of carbon dioxide, from 0 to 3% of ethane, from 0.3 to 50 parts by volume per million (vpm) of a reaction inhibitor or moderator of the halogenated hydrocarbon type, the remainder being argon and/or nitrogen and/or methane. The absolute pressure of the reactive gas current in the tube reactor may be chosen in a range of from 0.1 to 4 MPa, preferably from 1 to 3 MPa. The volume space hour velocity (VSHV) of the reactive gas current in the reaction tubes may be chosen in a range of from 1000 to 10 000 h<sup>-1</sup> (m<sup>3</sup> per m<sup>3</sup>.h of catalyst), preferably from 2000 to 8000 h<sup>-1</sup>, measured in standard temperature and pressure conditions.

The reactive gas current may with advantage be pre-heated to a temperature of from 100 to 200 °C, preferably from 140 to 190 °C. The temperature of the reactive gas current in the reaction tubes may be chosen in a range of from 140 to 350 °C, preferably from 180 to 300 °C, more particularly from 190 to 280 °C. Owing to the process of the invention, the temperature of the reactive gas current at the inlet of the reaction tubes may rise very rapidly or so to speak instantaneously to a temperature equal to or more than 210 °C. It may then continue to increase, but far more moderately, and attain a maximum temperature of at most equal to 270 °C, preferably at most equal to 265 °C, more particularly at most equal to 260 °C, in particular over a portion of the length of the tubes capable of extending from the first quarter to the fourth fifth, preferably from the first half to the third quarter of the length of the tubes in the flow direction of the reactive gas current. At the outlet of the reaction tubes, the temperature of the gas current resulting from the reaction may remain at said maximum temperature or, preferably, may decrease to a temperature equal to or less than 250 °C, preferably 240 °C, more particularly 230 °C, for example in a range of from 180 to 250 °C, preferably from 190 to 240 °C, more particularly 200 to 230 °C.

It is particularly advantageous to note that, owing to the process of the

invention, the exchange of heat along the reaction tubes makes it possible to combine a relatively stable reaction temperature profile and a maximum quantity of catalyst used in optimum activity conditions (the whole length of the tubes and more particularly in the zone situated towards the outlet of the tubes) per unit of internal tube volume available in the reactor. Said combination makes it possible to prevent a not inconsiderable portion of the reaction tubes being sacrificed to something other than the production of ethylene oxide and the maintenance of the catalyst charge in the tubes, more particularly by an absence of the catalyst, with the sole aim of controlling the heat exchanges and preventing hot spots. One of the major advantages of the process of the invention may further come from the fact that the temperature of the gas current resulting from the reacting at the outlet of the reaction tubes may be substantially reduced by at least 5 °C, for example by at least 10 °C, compared with the conventional processes. The result of said substantial reduction in the temperature is that all other conditions being equal, such as an identical concentration of molecular oxygen in the gas current, the limits of flammability of said current may be distanced accordingly and may thus permit a far safer process to be provided without in so doing sacrificing the yield and the selectivity of the reacting to ethylene oxide.

The bundle of reaction tubes is immersed in a heat exchange fluid which may be chosen in particular from among organic heat carrying fluids and water superheated under pressure (that is to say water at saturation temperature). The organic heat carrying fluids may be mixtures of oils or hydrocarbons such as linear or branched alkanes having in particular a boiling point higher than the maximum reaction temperature. It is possible to use the organic heat carrying fluids at a relative pressure of from 100 to 1500 kPa, preferably from 200 to 800 kPa, more particularly from 200 to 600 kPa. The organic heat carrying fluids may be chosen in particular from "Isopar"® of Exxon, "Therminol"® of Monsanto and "Dowtherm"® of Dow Chemicals. They may be used according to a process and a heat exchange apparatus as described in European patent application EP 0 821 678, in particular in Figure 1 or 2, or else in American patent US 4 759 313. The heat exchange fluid may also be water superheated under pressure, in particular used at a relative pressure of from 1500 to 8000 kPa. In this case, the superheated water may be used according to a

process and a heat exchange apparatus as described in American patent US 5 292 904. The temperature of the heat exchange fluid at the outlet of the tube reactor generally lies between 210 and 300 °C, preferably between 220 and 280 °C, more particularly between 210 and 280 °C. The temperature of the heat exchange fluid at the inlet of the tube reactor generally lies between 120 and 250 °C, preferably between 130 and 240 °C, more particularly between 130 and 230 °C.

The process of the invention may with advantage be carried out continuously, more particularly by utilising continuously the reactive gas current which flows successively and continuously through the three chambers of the tube reactor and by recovering continuously at the outlet of the reactor the gas current resulting from the reaction and containing the ethylene oxide.

Figure 1 is a diagrammatic representation of a tube reactor as used in the process of the invention. The tube reactor is of the vertical shell-and-tube exchanger type. The reactor contains three successive and adjacent chambers: an inlet chamber (1), then a central chamber (2) and an outlet chamber (3). There issues into the inlet chamber (1) a pipe (4) for the feeding of a reactive gas current containing ethylene and molecular oxygen. The central chamber (2) comprises a bundle of reaction tubes (5) parallel and identical to one another, and preferably cylindrical, each tube (5) containing in inlet (6) issuing into the inlet chamber (1) and an outlet (7) issuing into the outlet chamber (3). The reaction tubes (5) are filled with a solid silver-based catalyst (8) (shown tinted grey) over the whole or almost the whole of the length of the tubes (with the exception of a device for supporting the catalyst charge in the tube, such as a grille or a spring, not shown in Figure 1). The area of the internal cross-section of each reaction tube (5) decreases discontinuously between the inlet (6) and the outlet (7) of the tubes, by three successive stages (9), so that each reaction tube (5) is composed of four successive and contiguous tubular sections (10), each having an increasingly reduced internal cross-sectional area from the inlet (6) to the outlet (7). The reaction tubes (5) are immersed in a heat exchange fluid (11) which is introduced into the central chamber (2) through a pipe (12) for the feeding of fluid and which is drawn off from the central chamber (2) through a discharge pipe (13). The outlet

chamber (3) is provided with a pipe (14) for discharge of the gaseous current resulting from the reaction and containing the ethylene oxide.

Figures 2<sub>A</sub> and 2<sub>B</sub> are diagrammatic representations of the reaction tubes (5) capable of being used in the tube reactor shown in Figure 1 and enabling the process of the invention to be carried out. The elements of Figures 2<sub>A</sub> and 2<sub>B</sub> identical to those shown in Figure 1 are marked with the same numerical references. Figure 2<sub>A</sub> represents diagrammatically a reaction tube (5) which is provided with an inlet (6) and an outlet (7), and which has an internal cross-sectional area which decreases continuously from the inlet (6) to the outlet (7). Figure 2<sub>B</sub> represents diagrammatically a reaction tube (5) provided with an inlet (6) and an outlet (7). The area of the internal cross-section of the reaction tube (5) decreases continuously over a portion (15) of the length of the tube, and remains constant over the remaining upstream portion (16) situated towards the inlet (6) and over the remaining downstream portion (17) situated towards the outlet (7). The reaction tubes (5) as shown in Figures 2<sub>A</sub> and 2<sub>B</sub> are represented empty and without the catalyst (8) as represented in Figure 1.

Figure 3 is a diagrammatic representation of a reaction tube (5) capable of being used in the tube reactor shown in Figure 1 according to the process of the invention. The elements of Figure 3 identical to those shown in Figure 1 are marked with the same numerical references. The reaction tube (5) is provided with an inlet (6) and an outlet (7). The area of the internal cross-section of the reaction tube (5) decreases discontinuously between the inlet (6) and the outlet (7), by two successive stages (9), so that the reaction tube (5) is composed of three successive and contiguous tubular sections (10), each having an increasingly reduced internal cross-sectional area from the inlet (6) to the outlet (7). The reaction tube (5) as shown in Figure 3 is shown empty and without the catalyst (8) as represented in Figure 1.

Figures 4<sub>A</sub> and 4<sub>B</sub> are diagrammatic representations of the reaction tubes (5) capable of being used in the tube reactor shown in Figure 1 and enabling the process of the invention to be carried out. The elements of Figures 4<sub>A</sub> and 4<sub>B</sub> identical to those shown in Figure 1 are marked with the same numerical references. Figure 4<sub>A</sub>

represents diagrammatically a reaction tube (5) of cylindrical shape which is provided with an inlet (6) and an outlet (7). The area of the circular internal cross-section of the tube decreases discontinuously between the inlet (6) and the outlet (7), by two successive stages (9), so that the reaction tube (5) is composed of three successive and contiguous cylindrical tubular sections (10), each having an increasingly reduced internal diameter ( $D_i$ ) from the inlet (6) to the outlet (7). The reaction tube (5) possesses an external diameter ( $D_e$ ) which remains constant between the inlet (6) and the outlet (7). The reaction tube (5) may be in practice composed of three cylindrical and coaxial tubes ( $10_A$ ,  $10_B$  and  $10_C$ ) inserted into one another, so that in particular the external surface [of the] tube  $10_B$  is contiguous with the internal surface of the tube  $10_A$  and the external surface of the tube  $10_C$  is contiguous with the internal surface of the tube  $10_B$ . Figure  $4_B$  represents diagrammatically a reaction tube (5) of cylindrical shape which is provided with an inlet (6) and an outlet (7). The reaction tube (5) possesses an internal diameter ( $D_i$ ) which decreases continuously over a portion (15) of the length of the tube, and which remains constant over the remaining upstream portion (16) situated towards the inlet (6) and over the remaining downstream portion (17) situated towards the outlet (7). The reaction tube (5) possesses an external diameter ( $D_e$ ) which remains constant between the inlet (6) and the outlet (7). The reaction tube (5) may be in practice composed of two cylindrical and coaxial tubes ( $16_A$  and  $17_A$ ) inserted into one another, so that in particular the external surface of the tube ( $17_A$ ) is contiguous with the internal surface of the tube ( $16_A$ ). The tube ( $17_A$ ) is prolonged and contiguous with a tube ( $15_A$ ) coaxial with the two tubes ( $16_A$  and  $17_A$ ). The tube ( $15_A$ ) has a cylindrical external wall whose surface is contiguous with the internal surface of the tube ( $16_A$ ), and a revolving truncated internal wall whose large base contiguous with the tube ( $17_A$ ) has a diameter identical to the internal diameter of the tube ( $17_A$ ) and whose small base has a diameter identical to the internal diameter ( $D_i$ ) of the tube ( $16_A$ ). The reaction tubes (5) as shown in Figures  $4_A$  and  $4_B$  are represented empty and without the catalyst (8) as represented in Figure 1.

The process of the present invention offers in particular the following advantages:

- a substantially increased selectivity of the reacting to ethylene oxide for one and the same level of production of ethylene oxide, for example of at least 3 points (expressed in %);
- a clearly increased production of ethylene oxide by unit of internal tube volume available in a tube reactor;
- a maximum charge of active catalyst in the production of ethylene oxide per unit of internal tube volume available in a tube reactor;
- a relatively stable reaction temperature profile the whole length of the reaction tubes;
- a substantially reduced temperature at the outlet of the reaction tubes compared with that of the conventional processes;
- a safer process for manufacturing ethylene oxide by virtue of operating conditions which are further distanced from the flammability conditions of the gas current;
- a substantial decrease in the quantity of carbon dioxide produced compared with that of ethylene oxide, and a marked reduction in the discharges of carbon dioxide into the environment.

The selectivity of the reacting to ethylene oxide (expressed in %) may be calculated according to the following equation:

$$(1) \quad \text{Selectivity} = 100 \times (\text{molar production of ethylene oxide}) / (\text{molar consumption of ethylene})$$

The following examples illustrate the present invention.

### Example 1

The manufacture of ethylene oxide is carried out continuously in a tube reactor as shown in Figure 1, comprising an inlet chamber (1), a central chamber (2) and an outlet chamber (3). The central chamber (2) comprises a bundle of 3709 cylindrical reaction tubes, identical and parallel to one another. Each reaction tube (5), as shown

diagrammatically in Figure 3, comprises two successive stages (9), such that the tube (5) is composed of three successive and contiguous cylindrical tubular sections (10), each having a length (L) and an internal diameter (Di) decreasing between the inlet (6) and the outlet (7). The length (L) and the internal diameter (Di) of the three sections (10) have successively from the inlet (6) and the outlet (7) of the tubes the following values: L = 5 m and Di = 51.2 mm; L = 5 m and Di = 38.4 mm; L = 2 m and Di = 25.6 mm. The reaction tubes (5) are filled with a silver-based supported catalyst, in an equal manner between one another and over almost the whole (96%) of their length (only a last portion 0.5 m in length situated just before the outlet (7) being occupied by a spring for supporting the catalyst in the tube). The catalyst is a catalyst containing 14.7% by weight of silver supported on alumina. The total volume of the catalyst introduced into the reaction tubes of the reactor is about 62.5 m<sup>3</sup>.

There is introduced continuously into the tube reactor a reactive gas current containing by volume 28.2% of ethylene, 6.5% of molecular oxygen, 5% of carbon dioxide, 4.7% of nitrogen, 5.5% of argon, 0.3% of ethane, 4.8 vpm of ethyl chloride, the remainder being methane, at a flow rate of 270.8 tonnes/hour, at an absolute pressure of 2.06 MPa, the gas current being pre-heated to about 150 °C. Replenishments with fresh constituents of the reactive gas current, more particularly with fresh ethylene and oxygen, are carried out continuously to enable the composition of said current to be kept constant during the production. The bundle of reaction tubes is immersed in water superheated to 210 °C (at saturation temperature). The temperature of the reactive gas current is measured along the reaction tubes, which makes it possible, according to the graph shown in Figure 5, to draw a curve (1) plotting the temperature of the gas current as a function of the length of the tube (5) starting from the inlet (6).

Five tests are conducted in said conditions, in which the rates of introduction of fresh constituents of the reactive gas current, more particularly of fresh ethylene and oxygen, are changed for each of them. This is so as to obtain for each test a production (P) of ethylene oxide, expressed in tonnes of ethylene oxide per day, and there is calculated for each production (P) thus obtained the selectivity (S) of the

reacting to ethylene oxide (expressed in %) according to equation (1) mentioned above. The results of said tests are listed in Table 1 and enable a curve (1) to be drawn according to the graph shown in Figure 6 linking the selectivity (S) to the production (P) of ethylene oxide.



Table 1: Selectivity (S) as a function of the production (P) of ethylene oxide

Example 1	Test	Selectivity (S) (%)	Production (P) (t/d)
	1	83.2	256
	2	82.1	275
	3	81.0	290
	4	79.8	302
	5	78.5	314

5           Example 2

Exactly the same procedure is adopted as in Example 1, except that the tube reactor comprises a bundle of 2760 cylindrical reaction tubes (5), identical and parallel to one another, and that each tube (5) as shown in Figure 3 comprises two successive stages (9), so that the tube is composed of three successive and contiguous cylindrical tubular sections (10), each having a length (L) and an internal diameter (Di) decreasing between the inlet (6) and the outlet (7). The length (L) and the internal diameter (Di) of the three sections (10) have successively from the inlet (6) and the outlet (7) of the tubes the following values: L = 5 m and Di = 64.0 mm; L = 5 m and Di = 38.4 mm; L = 2 m and Di = 25.6 mm. The reaction tubes are filled with the silver-based catalyst, as in Example 1, in an equal manner between one another and over almost the whole (96%) of their length. The total volume of the catalyst introduced into the reaction tubes of the reactor is substantially identical to that of Example 1.

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Three tests are conducted in said conditions, in which the rates of introduction of fresh constituents of the reactive gas current, more particularly of fresh ethylene and oxygen, are changed for each of them. This is so as to obtain for each test a production (P) of ethylene oxide, expressed in tonnes of ethylene oxide per day, and there is calculated for each production (P) thus obtained the selectivity (S) of the

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reacting to ethylene oxide (expressed in %) according to equation (1) mentioned above. The results of said tests are listed in Table 2 and enable a curve (2) to be drawn according to the graph shown in Figure 6 linking the selectivity (S) to the production (P) of ethylene oxide.

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Table 2: Selectivity (S) as a function of the production (P) of ethylene oxide

Example 2	Test	Selectivity (S) %	Production (P) (t/d)
	1	81.7	277
	2	80.4	299
	3	78.9	315

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Example 3 (comparative)

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Exactly the same procedure is adopted as in Example 1, except that the tube reactor comprises a bundle of 4750 cylindrical reaction tubes (5), identical and parallel to one another, and that each tube (5) has a conventional shape and possesses in particular an internal diameter (Di) which is constant between the inlet (6) and the outlet (7) of the tubes and which is equal to 38.7 mm, and a length (L) of 12 m. The reaction tubes are filled with the silver-based catalyst, as in Example 1, in an equal manner between them and over almost the whole (96%) of their length. The total volume of catalyst introduced into the reaction tubes of the reactor is substantially identical to that of Example 1.

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The temperature of the reactive gas current is measured along the reaction tubes, which enables a curve (2) to be drawn according to the graph shown in Figure 5 plotting the temperature of the gas current as a function of the length of the tube (5) starting from the inlet (6).

Five comparative tests are conducted in said conditions, in which the rates of introduction of fresh constituents of the reactive gas current, more particularly of fresh ethylene and oxygen, are changed for each of them. This is so as to obtain for each test a production (P) of ethylene oxide (expressed in tonnes of ethylene oxide per day), and there is calculated for each production (P) thus obtained the selectivity (S) of the reacting to ethylene oxide (expressed in %) according to equation (1) mentioned above. The results of said tests are listed in Table 3 and enable a curve (3) to be drawn according to the graph shown in Figure 6 linking the selectivity (S) to the production (P) of ethylene oxide.

Table 3: Selectivity (S) as a function of the production (P) of ethylene oxide

Example 3 (comparative)	Test	Selectivity (S) (%)	Production (P) (t/d)
	1	83.8	235
	2	82.8	248
	3	81.8	257
	4	80.8	266
	5	79.7	275

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An analysis of the results given in Tables 1, 2 and 3 and in the graphs of Figures 5 and 6 shows that:

(a) according to the process of the invention, the reaction temperature profile along the tubes is relatively stable between the inlet and the outlet of the tubes (curve (1) of Figure 5), compared with the temperature profile obtained with conventional reaction tubes (curve (2) of Figure 5); thus according to the invention, in the inlet zone of the tubes the temperature rises far quicker and attains very rapidly the temperature at which the catalytic reaction for the formation of ethylene oxide starts; thereafter the temperature continues to increase progressively and attains a maximum value of close to 250 °C and then decreases slightly to about 215 °C, in particular in

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the outlet zone of the tubes, which thus makes it possible to distance the operating conditions from the maximum flammability zone of the gaseous mixture, and nevertheless gives the catalyst an opportunity to continue to produce ethylene oxide with a good selectivity;

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(b) the selectivity (S) of the reacting to ethylene oxide for a given production (P) of ethylene oxide is, owing to the process of the invention, higher (curves (1) and (2) of Figure 6) than the selectivity (S) obtained according to a conventional process, all other things being equal (curve (3) of Figure 6).

BPCL 9946 / B 431 (1)

Claims

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1. Process for manufacturing ethylene oxide by the catalytic oxidation reacting of ethylene by molecular oxygen in a tube reactor comprising three successive and adjacent chambers through which passes a reactive gas current containing ethylene and molecular oxygen, an inlet chamber of the reactive gas current, then  
10 a central chamber forming the ethylene oxide in a gas current resulting from the reacting, and an outlet chamber of the resulting gas current, the central chamber comprising a bundle of reaction tubes immersed in a heat exchange fluid and filled with a solid silver-based catalyst in contact with which the reactive gas current forms the ethylene oxide, each reaction tube possessing an inlet issuing  
15 into the inlet chamber and an outlet issuing into the outlet chamber, the process being characterised in that the area of the internal cross-section of the reaction tubes decreases between the inlet and the outlet of the tubes over at least a portion of the length of the tubes and remains constant over any remaining portion.
- 20 2. Process according to claim 1, characterised in that the area of the internal cross-section of the reaction tubes decreases continuously.
3. Process according to claim 1, characterised in that the area of the internal cross-section of the reaction tubes decreases discontinuously, more particularly by  
25 stages.
4. Process according to any one of claims 1 to 3, characterised in that the area of the internal cross-section (A1) at the inlet of the reaction tubes is from 1.5 to 12 times, preferably from 2 to 10 times, in particular from 3 to 9 times greater than  
30 the area of the internal cross-section (A2) at the outlet of said tubes.
5. Process according to any one of claims 1 to 4, characterised in that the decrease in the area of the internal cross-section of the reaction tubes is effected once only

over the length of the tubes, either continuously over a portion of the length of the tubes, or discontinuously, in particular by a stage, such a decrease being effected at the latest before the last fifth of the length of the tubes which is situated towards the outlet.

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6. Process according to any one of claims 1 to 4, characterised in that the decrease in the area of the internal cross-section of the reaction tubes is effected two or more successive times over the length of the tubes, either continuously over two or more portions of the length of the tubes, or discontinuously, in particular by  
10 two or more successive stages, such a decrease being effected for the first time at the latest before the last fifth of the length of the tubes which is situated towards the outlet.

7. Process according to any one of claims 1 to 6, characterised in that the reaction  
15 tubes have a length (L) of from 6 to 20 m, preferably from 8 to 15 m, an area of the internal cross-section (A1) at the inlet of the tubes of from 12 to 80 cm<sup>2</sup>, preferably from 16 to 63 cm<sup>2</sup>, and an area of the internal cross-section (A2) at the outlet of the tubes less than A1 and ranging from 1.2 to 16 cm<sup>2</sup>, preferably from 1.8 to 12 cm<sup>2</sup>.

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8. Process according to any one of claims 1 to 7, characterised in that the reaction tubes have a cylindrical shape and exhibit a circular internal cross-section whose internal diameter (Di) decreases between the inlet and the outlet of the tubes over at least a portion of the length of the tubes and remains constant over any  
25 remaining portion.

9. Process according to claim 8, characterised in that the internal diameter (D1i) at the inlet of the reaction tubes is from 1.2 to 3.5 times, preferably from 1.4 to 3.1 times, in particular from 1.7 to 3 times higher than the internal diameter (D2i) at  
30 the outlet of said tubes.

10. Process according to claim 8, characterised in that the reaction tubes have a

length (L) of from 6 to 20 m, preferably from 8 to 15 m, an internal diameter (D1i) at the inlet of the tubes of from 38 to 100 mm, preferably from 45 to 90 mm, and an internal diameter (D2i) at the outlet of the tubes less than D1i and ranging from 12 to 45 mm, preferably from 15 to 40 mm.

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11. Process according to any one of claims 1 to 10, characterised in that the reaction tubes have a wall whose thickness is constant from the inlet up to the outlet of the tubes.

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12. Process according to any one of claims 1 to 10, characterised in that the reaction tubes have a wall whose thickness varies from the inlet up to the outlet of the tubes.

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13. Process according to any one of claims 8 to 10, characterised in that the reaction tubes have an external diameter which is constant between the inlet and the outlet of the tubes and preferably equal to the external diameter at the inlet of said tubes.

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14. Process according to any one of claims 1 to 13, characterised in that the heat exchange fluid immersing the bundle of reaction tubes is chosen from among water superheated under pressure and organic heat carrying fluids, in particular mixtures of oils or hydrocarbons.

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15. Process according to claim 14, characterised in that the organic heat carrying fluid is used at a relative pressure of from 100 to 1500 kPa, preferably from 200 to 800 kPa, in particular from 200 to 600 kPa.

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16. Process according to claim 14, characterised in that the superheated water is used at a relative pressure of from 1500 to 1800 kPa.

17. Process according to any one of claims 1 to 16, characterised in that the temperature of the reactive gas current in the reaction tubes is chosen in a range

of from 140 to 350 °C, preferably from 180 to 300 °C, in particular from 190 to 280 °C.

- 5 18. Process according to any one of claims 1 to 17, characterised in that the reactive gas current is pre-heated to a temperature of from 100 to 200 °C, preferably from 140 to 190 °C.
- 10 19. Process according to any one of claims 1 to 18, characterised in that the temperature of the gas current resulting from the reacting at the outlet of the reaction tubes remains at a maximum temperature attained by the reactive gas current in the reaction tubes or preferably decreases to a temperature equal to or less than 250 °C, preferably 240 °C, more particularly 230 °C, in particular a temperature chosen in a range of from 180 to 250 °C, preferably from 190 to 240 °C, more particularly from 200 to 230 °C.



Received on 23/01/03



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<b>Your file references</b> <i>(optional)</i>		9446/B431
<b>NATIONAL REGISTRATION N°</b>		0 216 145
<b>TITLE OF THE INVENTION (200 characters or spaces maximum)</b>  PROCESS FOR MANUFACTURING ETHYLENE OXIDE		
<b>THE APPLICANT(S):</b>  BP LAVERA S.N.C. and BP CORPORATION NORTH AMERICA, Inc.		
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